Coordination of iron in E-glass

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Iron is usually present in glasses either as an impurity from the raw materials used or as an additive. Its presence confers on the glass a number of properties, notably colour [1] and magnetism [2–4]. E-glass, which has 0.3% Fe_2O_3, was in rod form a pale green colour which is due to iron ions. Iron is used alone or in combination in the commercial production of green-coloured glass. Most of the oxides of the first series of transition metals produce a strong colour when present in an oxide glass at a concentration of less than 1 %. These transition metal ions are incorporated in the glass structure each being surrounded by oxygen anions and are also responsible for the paramagnetism in glasses. This letter reports on the coordination of iron in E-glass. It was of interest to use magnetic measurements to detect iron because the objective was to eliminate Fe_2O_3 (and all other oxides) to obtain high-purity silica. The starting material was E-glass of the composition, 54.2 wt% SiO_2, 14.0 wt% Al_2O_3, 19.8 wt % CaO, 2.2 wt% MgO, 8.2 wt% B_2O_3, 0.3 wt% Fe_2O_3 and 0.56 wt % $Na_2O + K_2O$. This was leached in HCI in order to obtain 98% silica. A complete description of the process as well as the changes in physical properties as a result of leaching have been given previously [5–10].

The magnetism in E-glass is due entirely to the presence of iron as there are no other transition metal ions. In the present study, fine powdered samples of E-glass were used to measure the magnetic susceptibility using the standard Gouy method. It was found to be 0.6017 $\times 10^{-6}$/g ion. From this value the magnetic moment can be calculated to be 5.8 Bohr magnetons. It is known [4] that a value of 5.90 Bohr magnetons indicates that the iron atom is the ferric state.

It was found that the gram suceptibility decreased with leaching time. The glass sample when leached in 4N HCl for different periods of time at 100° C loses the paramagnetism and becomes diamagnetic. The values were found to be 0.1217 $\times 10^{-6}$/g ion at 0.5 h and 0.0236 $\times 10^{-6}$/g ion at 1 h. After 2 h of leaching, the material became diamagnetic. The decrease in gram susceptibility is due to the removal of paramagnetic centres, namely Fe^{3+} ions, by hydrochloric acid. The paramagnetism introduced into a glass by the incorporation of iron ions, arises from the unpaired electrons of the unfilled 3d subshell of this element. The contribution of electrons to magnetic properties is strongly influenced by the surrounding electrostatic fields [11].

Iron can be in fourfold or sixfold coordination [12, 13] which can be confirmed by Mossbauer [14] or ESR spectroscopy. We used the latter method at a frequency of 9.49 GHz. Initially the field was set at 3250 G and the scan range was 2000 G (i.e. 2250 to 4250 G). To the powdered sample of E-glass, reference material diphenyl dipicryl hydrazine (DPPH) was also added. But for the DPPH peak, no other peak was observed. If iron were present in sixfold coordination a peak would have appeared at 3250 G. The field range was then increased to 4000 G and the field was set at 2200 G (i.e. 200 to 4200 G). A single peak was observed, as shown in Fig. 1, at 1600 G indicating that the only species present is iron with a four-fold coordination. Previous work has shown that in sodium silicate glass, $g = 2$ resonance indicates that the Fe^{3+} is in six-fold coordination (or as a network modifier) and that $g = 4.28$ resonance shows that Fe^{3+} ion is in four-fold coordination (or as a network former) [15, 16]. The g value of 4.28 corresponds to the field (H) value of 1600 G and $g = 2$ corresponds to H of 3250 G. The observed peak thus indicates the presence of Fe^{3+} in four-fold coordination. Fig. 1 shows the ESR spectra of E-glass in three conditions (i) unleached, (ii) leached in 4N HCl for various times and (iii) leached in 0.1 N HCI for 2 h. Both in untreated and mildly treated E-glass the 1600 G peak is present, the peak height decreasing with leaching

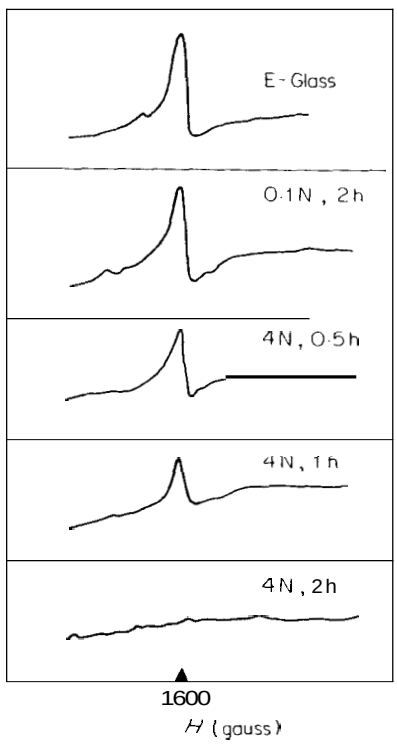

Figure 1 ESR spectra of E glass and leached E glass.

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time. But with severe treatment the peak disappears completely.

The conclusions are (a) the **ESR** measurements show that Fe^{3+} ion is present in E-glass in four-fold coordination and has the role of a network former. (b) Iron oxide can be removed completely from the E-glass by leaching with **4** N **HCI** for 2 h and the glass becomes diamagnetic as shown **by** both **ESR** and magnetic susceptibility measurements.

References

1. C. R. BAMFORD, **"Colour Generation and Control in Glass"** (Elsevier, **New York,** 1977).
2. G. W. MOREY, **"The Properties of Glass" 2nd edn (Reinhold, New York, 1954).**
3. H. COLE, *J. Soc. Glass Technol.* **34** (1950) 220.
4. C. R. BAMFORD, *Phys. Chem. Glasses 35* (1957) 25.
5. B. E. RAMACHANDRAN, B. C. PAI and N. BALASUERAMANIAN, *J. Am. Ceram. Soc. 63* (1980) 1.
6. *Idem, J. Mater. Sci.* **14** (1979) 1572.
7. B. E. RAMACHANDRAN, B. C. PAI and N. BALASUBRAMANIAN, G. V. SUBHA RAO and G. ARAVAMUDAN, *ihid.* **16** (1981) 1611.
8. B. E. RAMACIIANDRAN. N BALASUBRAMANIAN, G. V. SUBHA RAO and G. ARAVAMUDAN, *Bull. Mater. Sci. 3* (1981) *333.*
9. B E. RAMACHANDRAN. B C. PAI and N BALASUBRAMANIAN, *Mater. Sci. Engng 43* (1980) 199.
10. B. E. RAMACHANDRAN and N BALASUBRAMANIAN, *J. Mater. Sci. Lett.* **4** (1985) 688.
11. H. R RAWSON, **"Properties and Applications of Glass",** Vol. 3 (Elsevier, New York, **1980).**
12. C. H. HIROYAMA, *Phys. Chem. Glasses* **9 (1968)** 109.
13. J. WONG and C A. ANGEL, **"Glass Structure by Spectroscopy" (Marcel-Dekker, New York,** 1976).
14. C. R. KURKJIAN. *J. Non Cryst. Solids3* (1970) 157.
15. R. F. TUCKER, **"Advances in Glass Technology". VI International Congress on Glass (Plenum, New York,** 1962) **p.** 103.
16. G. O. KARAPETYON, V. A. TSKHONSHI and D. M. YUDIN, *Sov. Phys. Solid State* **5** (1963) 456.

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